



Temperature-dependent formation of vertical concentration gradients in lead-acid batteries under PSoC operation – Part 1: Acid stratification

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ABSTRACT

In micro-hybrid vehicles, the starter battery is subject to heavy cyclic loads. Results of these cyclic loads are vertical concentration gradients (acid stratification). For this study, it was analyzed systematically how different temperatures influence the formation and reduction of acid stratification. To this end, flooded lead-acid batteries were cycled during a cycle test with 17.5% depth of discharge at -5°C , 3°C , 27°C , and 60°C . To determine the extent of acid stratification caused by the cycling, the acid density values of the test batteries cycled at four different temperatures were measured using acid density monitoring. The acid densities were measured hourly in 0%, 15%, 30%, 45%, 60%, 80%, and 100% sections in the direction of the perpendicular z-axis of the battery. The measurements showed that the extent of acid concentration gradients is dependent on the temperature, with acid stratification caused by an uneven distribution of current over the height of the plates. Furthermore, it was established that battery discharging as well as battery charging causes an inhomogeneous acid density distribution in the battery electrolyte.

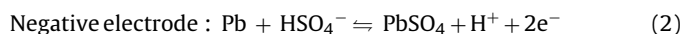
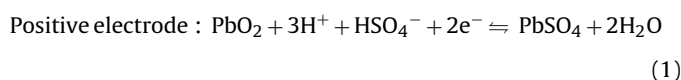
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1. Introduction

In 2008, transport was responsible for 20.2% of energy-related CO₂ emissions. In this figure, road transport accounted for over 19% [1]. For this reason, the automotive industry is focussed on developing alternative drive technologies to reduce fuel consumption. One of these alternative drive technologies is the micro-hybrid technology (i.e., automatic start–stop system and regenerative braking). Micro-hybrid vehicles have significantly lower fuel consumption and CO₂ emissions. However, the starter battery in micro-hybrid vehicles is subject to immense cyclic loads. In micro-hybrids, the much larger number of engine starts with additional battery discharges in the stop phases significantly raises the number of battery charging and discharging phases.

The sulfuric acid electrolyte in the lead-acid battery is both ion-conducting medium and reactant. Due to the participation of the electrolyte in the charging and discharging reaction (Eqs. (1) and (2)), the acid concentration changes depending on the state of charge [3]. The electrolyte density in a conventional vehicle battery

fluctuates between approx. 1.28 kg/L and 1.10 kg/L [2].



The increased charging and discharging phases to which batteries in micro-hybrid vehicles are subject facilitate the formation of concentration gradients, and, therefore density gradients in the electrolyte of the battery. In scientific literature, the occurrence of acid density gradients is attributed to acid of higher density produced during the charging process. A vertical concentration gradient is formed due to gravity. Often observed in practice and referred to as acid stratification [4], this causes a reduction in performance and premature aging of the battery.

When a vertical concentration gradient is present, the electromotive force on the electrodes increases from top to bottom. This is described by the Nernst equation. In areas of high electromotive force, the electrodes are discharged preferentially, causing lead sulfate crystals (PbSO₄ crystals) to form in the active compound. The number and size of these crystals is dependent on the sulfuric acid concentration and the temperature.

When the lead-acid battery is charged and discharged, it undergoes what is called dissolution–precipitation. The thermodynamics and kinetics of the crystal dissolution and precipitation of lead

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sulfate directly influence the speed of the charging and discharging reactions. In other words, these factors affect the current draw and discharge characteristics of the battery [5–7].

In practice, the starter battery and, therefore, the electrolyte are subject to temperature fluctuations. This is caused by weather conditions and the installation location of the battery in the vehicle. When the starter battery is installed in the engine compartment, it can be exposed to temperatures of more than 60 °C in temperate climate zones.

The Arrhenius equation defines that temperature is an important influencing variable in chemical reactions. At low temperatures and acid concentrations like those in discharged lead-acid batteries, the electrolyte can also freeze [2]. The discharging causes water to form in the pores of the electrodes, depending on the discharge current, which can freeze at low temperatures. The process is based on the formation of (in this case horizontal) acid concentration gradients and is known as ice passivation [8]. The ice formation is associated with a reduction in the conductivity of the electrolyte.

At low temperatures, the charging and discharging reactions (Eqs. (1) and (2)) are impeded [2]. The reason for this are, besides the poorer conductivity of the electrolyte, the reduced solubility of the lead sulfate and the less effective transport of the reactants to the surface of the electrodes, as well as the increased incidence of competing secondary reactions (production of hydrogen).

At high temperatures, accelerated diffusion processes speed up the discharging and charging reaction. Furthermore, the electrical conductivity of the electrolyte increases [2]. But also here, competing reactions occur alongside the charging and discharging reactions (production of hydrogen, corrosion on the positive electrode).

The relationships between acid concentration, temperature and battery life have been demonstrated in a number of papers. Hattori et al. [9] examined how higher acid concentrations affect the cycle life of lead-acid batteries. Bullock [10] analyzed how acid concentration and temperature affect the drying-out of VRLA batteries (VRLA = Valve regulated lead-acid batteries). Pavlov et al. studied the influence of sulfuric acid concentration on the behavior of the positive [11] and negative electrodes [12] of lead-acid batteries.

For this study, it was analyzed systematically how different temperatures influence the formation of acid stratification during cycling of the partially discharged battery in the vehicle environment. The PSoC operation in micro-hybrid vehicles was simulated using the battery cycles described in [13,14] with 17.5% depth of discharge, which provokes the formation of acid stratification in the electrolyte of the respective battery sample. 17.5% depth of discharge is around one-sixth of a full discharge and has been proven to be a realistic depth of discharge to give in reasonable time results corresponding to loads as typically seen in start/stop vehicles without producing artifacts due to too high discharge (as would be the case for even higher depths of discharge) [14].

2. Experimental

2.1. Battery samples

All investigations were done with commercial flooded 12V72Ah PbCa batteries produced by company MOLL. These batteries were designed after Volkswagen specifications VW TL 75073 and 82506. The 7 positive electrodes per cell consisted of cast grid plates, 8 negative electrodes were made of expanded metal. These batteries were cycled with 17.5% depth of discharge at temperatures of –5 °C (battery 1), 3 °C (battery 2), 27 °C (battery 3), and 60 °C (battery 4). The batteries had a standardized design (LN3 battery boxes, as per EN 50342-1 [15]). To characterize the battery samples, the

Table 1

OCV [V], R_i [mΩ], and weight [kg] of the battery samples.

	OCV [V]	R_i [mΩ]	Weight [kg]
Battery 1	12.90	3.66	20.13
Battery 2	12.90	3.76	19.76
Battery 3	12.90	3.77	20.23
Battery 4	13.09	3.66	20.24

open-circuit voltage (OCV), internal resistance (R_i) (using a Hioki 3554 internal resistance meter), and the weight of the respective batteries were determined before the start of the test (Table 1).

2.2. Electrical tests

The electrical battery tests were performed using the cycle and ICC 1000/20 (model ABR) test systems in constant temperature water baths (3 °C, 27 °C, and 60 °C) or a climate chamber (–5 °C). The batteries were first pre-conditioned in an initial test (Section 2.2.1). After the batteries had been discharged to 50% State of Charge (SOC), they were cycled with 17.5% depth of discharge (Section 2.2.2).

The current (I , in [A]) and capacity (K , in [Ah]) were used in the standard form (K_{20} or I_{20}) for lead-acid starter batteries. The definitions of these characteristics are as follows:

- K_{20} The battery capacity [Ah] is the amount of electricity that is assigned to a battery. It must be possible to draw this with a defined current I_{20} (nominal discharge current) in 20 h up to a defined discharge voltage of 10.5 V at (27 + 0/–2) °C. $K_{20} = I_{20} \cdot 20$ (with K in [Ah]; I in [A]).
- I_{20} The nominal discharge current in [A] is the discharge current assigned to the battery capacity K_{20} delivered by the battery during the defined discharging duration. $I_{20} = K_{20}/20$.

2.2.1. Initial tests

The cycle and ICC 1000/20 test systems from ABR were used for the initial measurements. The capacities and the cold-start characteristics of the individual battery samples were determined as per EN-50342-1 [15]. The batteries were tested in the sequence K_{20} – charging – cold start – recharging. This test sequence was repeated three times, but without cold cranking test in the last sequence.

2.2.2. Battery cycling

For the cycling, the test batteries were conditioned to the respective test temperature over approx. 24 h and cycled with a 17.5% depth of discharge as per the test sequence detailed in Table 2. A cycling unit (=continuous testing unit, CTU) consists of 85 cycles. The batteries were cycled until failure.

The charging voltage used in the cycles was selected depending on the temperature. The charging voltage was 15 V for batteries 1 and 2, 14.4 V for battery 3, and 14 V for battery 4. As in the cycles, the charging voltage in the equalization charges and recharges was also adjusted to the temperature (Table 2).

2.3. Acid density measurements

To determine the extent of acid stratification caused by the cycling, the acid density values of the four test batteries were measured using acid density monitoring (ADM) [16]. The acid densities were measured hourly in 0%, 15%, 30%, 45%, 60%, 80%, and 100% sections in the direction of the perpendicular z-axis of the battery (Fig. 1) after cycling, after the equalization charge L_{18h} , after the 20 h discharge E , and after the recharge L_{23h} . Measuring instrument was a Mettler Toledo Densito 30PX acid densitometer. For experimental reasons, measurement of the acid concentration in the different sections was performed in selected cells of the battery. For this reason, individual cells were prepared for the measurement in specific, fixed sections. However, the acid density was also

Table 2

Cycling of the batteries with 17.5% depth of discharge, subsequent equalization charging (L_{18h}), capacity testing (E), and recharging (L_{23h}) (charging voltage and failure criterions valid for flooded lead-acid batteries).

	Measurement	Description of the test sequence
(a)	Battery state of charge (SOC) brought to 50%	2.5 h discharge with $4I_{20}$ Failure criterion: discharge voltage < 10 V
(b)	85 times: Charge Discharge	40 min $7I_{20}$ and 14.4 V 30 min $7I_{20}$ Failure criterion: discharge voltage < 10 V
(c)	Equalization charge (L_{18h})	18 h with $2I_{20}$ and 16.0 V
(d)	Capacity test (E)	Discharge with I_{20} (up to an end-of-discharge voltage of 10.5 V)
(e)	Recharge (L_{23h})	23 h with $2I_{20}$ and 16.0 V

measured at 0% and 100% immersion depth in all cells. For 0% and 100% immersion depth of the acid densitometer, the average acid density value (AV) was calculated using values from all six cells of the battery. The acid density measurements were performed after the first and the final testing unit of the cycle test, described under Section 2.2.2.

3. Results and discussion

To represent the acid density changes of the batteries cycled at different temperatures with regards to the temperature-dependent formation of stratification, the acid densities were monitored after the first and last CTUs of the cycling, during the subsequent equalization charging L_{18h} , the discharging E , and the recharging L_{23h} . To this end, the changes to acid densities and acid density differences in the cells between the area above the plates and the area at the base of the cells were determined for different temperatures over L_{18h} , E , and L_{23h} . Table 3 shows the changes in acid density differences $\Delta\rho$ ($\Delta\rho = 100\% \text{ AV} - 0\% \text{ AV}$) over the height of the cell, between start and end of a discharge/charge, for all tested sample batteries (batteries 1–4) at different temperatures. Both the values for the test sequence $L_{18h}/E/L_{23h}$ after the first cycling unit and the relevant values observed in the analogous test sequence after the last cycling unit are shown. The acid density difference $\Delta\rho$ at the start of each load (charging or discharging) is represented as $\Delta\rho_{\text{Start}}$. $\Delta\rho_{\text{End}}$ indicates the acid density difference at the end of a load. $\Delta\rho_{\text{Start}}$ at L_{18h} indicates additionally the acid density difference that has formed in the electrolyte over the 85 cycles of a cycling unit (CTU). $\Delta\rho_{\text{End}}$ after L_{18h} shows the acid density difference after the equalization charge. $\Delta\rho_{\text{Start}}$ at E specifies the acid density difference at the start of the discharge. $\Delta\rho_{\text{End}}$ shows the relevant acid

density difference at the end of the discharge E . The same applies for $\Delta\rho_{\text{Start}}$ and $\Delta\rho_{\text{End}}$ for L_{23h} . The difference between $\Delta\rho_{\text{Start}} - \Delta\rho_{\text{End}}$ indicates how much stratification was formed or reduced during L_{18h} , E , or L_{23h} . A positive sign (+) indicates an increase in stratification and a negative sign (–) indicates a decrease.

Figs. 2a, b and 3a, b show the change in acid density at different temperatures and at different plate heights (0% AV – average of acid density of all six cells | 15%, 30%, 45%, 60%, 80%, and 100%) – single value of one cell each | 100% AV – average of acid density of all six cells) during the processes L_{18h} , E and L_{23h} for the first CTU (Fig. 2) and the respective last CTU (Fig. 3). The x-axis indicates process time where $t=0$ is defined to be the start of L_{18h} . P displays pauses between the processes L_{18h} , E and L_{23h} (e.g. due to end of discharge at night). All acid densities were measured *in situ* and are exactly plotted at their measurement time.

In the following, the acid density results for different plate heights, processes (L_{18h} , E , and L_{23h}), and temperatures are analyzed and interpreted in context.

3.1. Formation of acid stratification after the first continuous testing unit

When observing the acid density differences in Table 3 and Fig. 2a and b, it is clear that stratification forms during cycling, at all temperatures. This effect is more pronounced at lower temperatures (-5°C , battery 1 and 3°C , battery 2). After the cycling (85 cycles, first CTU), the existing acid density difference ($\Delta\rho_{\text{Start}}$) in the electrolyte is the largest. Compared to the other batteries, battery 2 (3°C) shows the largest value for $\Delta\rho_{\text{Start}}$, in other words, the highest stratification (Table 3).

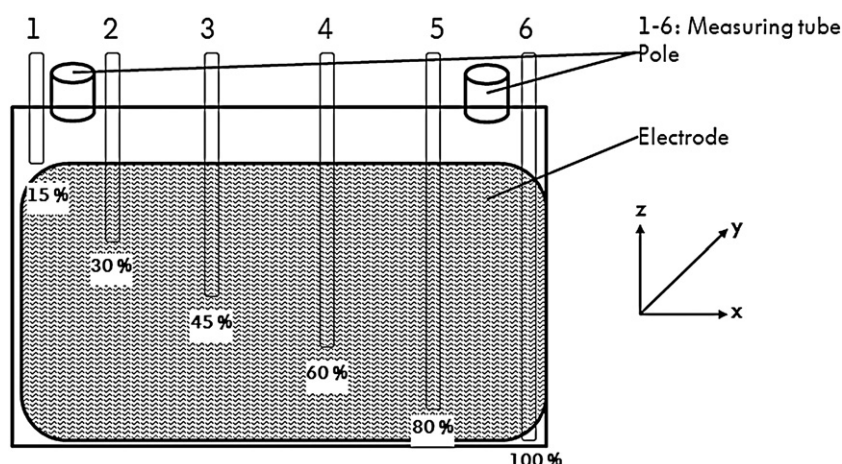


Fig. 1. Measuring tubes over the height of the battery electrode.

Table 3Acid density differences $\Delta\rho$ [mg cm⁻³] before ($\Delta\rho_{\text{Start}}$) and after ($\Delta\rho_{\text{End}}$) at L_{18h} , E , and L_{23h} , as well as the respective difference $\Delta\rho_{\text{Start}} - \Delta\rho_{\text{End}}$.

T [°C]	-5			3			27			60		
	L_{18h}	E	L_{23h}	L_{18h}	E	L_{23h}	L_{18h}	E	L_{23h}	L_{18h}	E	L_{23h}
<i>First CTU</i>												
$\Delta\rho_{\text{Start}}$ [mg cm ⁻³]	124	54	92	143	62	83	71	34	63	45	29	77
$\Delta\rho_{\text{End}}$ [mg cm ⁻³]	34	110	42	66	73	68	13	78	37	13	75	35
$\Delta\rho_{\text{Start}} - \Delta\rho_{\text{End}}$ [mg cm ⁻³]	-90	+56	-50	-77	+10	-15	-58	+44	-28	-32	+46	-42
<i>Last CTU</i>												
$\Delta\rho_{\text{Start}}$ [mg cm ⁻³]	85	52	103	104	51	69	37	21	19	128	12	96
$\Delta\rho_{\text{End}}$ [mg cm ⁻³]	37	124	50	27	79	53	12	20	19	13	100	15
$\Delta\rho_{\text{Start}} - \Delta\rho_{\text{End}}$ [mg cm ⁻³]	-48	+72	-53	-77	+28	-16	-25	+1	0	-115	+88	-81

During L_{18h} , the stratification in all batteries is reduced. This reduction is more effective when the temperature increases. The least significant reduction in acid concentration differences during L_{18h} can be observed in battery 2 (3 °C) (Table 3).

After L_{18h} , battery 2 shows a higher acid density difference (stratification) (Table 3) compared to battery 1 (-5 °C). The much lower acid density difference at high temperatures (27 °C, battery 3 and 60 °C, battery 4) during the first CTU of the cycle test is reduced further during L_{18h} (Table 3).

During L_{18h} , the acid densities change to different degrees over the height of the plates, depending on the temperature (Fig. 2a and b). At low temperatures (-5 °C, battery 1 and 3 °C, battery 2), a gradual convergence of the acid density values in the upper and lower plate regions is evident, caused by a predominant increase in the acid densities in the upper areas of the plate. At higher test temperatures (battery 3, 27 °C and battery 4, 60 °C), the acid density increases during L_{18h} over the entire height of the plate. Note that the acid concentrations measured over time at the individual points of the cell run through local maxima and minima, evidently dependent on the temperature and the measuring position. In the case of batteries 1 and 2 (-5 °C and 3 °C), a predominant increase in the acid densities in the upper plate areas is evident during the first I charging phase. After the I phase, batteries 1 and 2 show an increase in acid density values in the upper and middle plate areas (0–60%) with a simultaneous decrease in acid density values in the lower plate areas (80% and 100%) (Fig. 2a). This is probably a result of the homogenization of the electrolyte caused by gassing. Toward the end of L_{18h} , the acid densities in batteries 1 and 2 increase over the entire height of the plate. However, this increase is much less pronounced in the lower plate region (Fig. 2a). Here, differences were observed between battery 1 and battery 2, too. The lower the temperature, the lower the acid concentration at 100% and 80% immersion depth, and, consequently, the change during L_{18h} is also much less pronounced. As well as the homogenization caused by gassing, a second effect must be assumed for the change in distribution of acid concentration: the upper and lower plate areas are charged to different degrees. At the end of L_{18h} , distinct acid concentration gradients were still found in batteries 1 and 2 (Fig. 2a). At higher temperatures (battery 3, 27 °C and battery 4, 60 °C), the acid density values over the height of the plates are very close together (Fig. 2b). The main difference to charging at low temperatures is that, in the final hours, the acid concentration increases evenly over the entire height of the cells, and that, at the end of L_{18h} , there is scarcely any stratification in the cell (Fig. 2a).

While the stratification in batteries 1 and 2 barely changes during the subsequent pause P up to the start of discharging, it is important to note that the acid concentration differences of batteries 3 and 4 increase during P , between L_{18h} and E (Fig. 2b), especially due to an increase in the acid concentration in the lower plate areas. One explanation is that acid released from the pores of the electrodes after the end of charging sinks to the bottom of the cell, forming stratification during the pause.

Observation of the acid concentration distribution during E shows that stratification forms dependent on the temperature (Fig. 2a and b). After E , batteries 1, 3, and 4 show the highest stratification while battery 2 shows the lowest. Looking more closely at the acid density curves, we can see that the differences in the acid concentrations over the height of the plate decrease at the start of E , at all temperatures (Fig. 2a and b). This is in line with expectations, since acid stratification caused by electromotive force in the lower third of the plate should initially facilitate discharging in the lower plate area.

In the second half of E , though, the acid density differences over the height of the plate increase.

The observations up to this point show that, contrary to the previous theory, acid stratification is not a phenomenon caused solely by the concentrated acid formed during the charging process sinking to the lower plate areas from the upper areas. Since acid is consumed during the discharging process, the stratification formed during E can only be explained by the uneven amount of substance over the height of the plate. After the initial reduction of the stratification, the acid concentration gradients increase over the height of the plate as the discharging process continues. This is evident in the fact that further discharging is increasingly more difficult in the lower part of the plate, the reason being that the compound in the lower part of the plate must already be very deeply discharged (irreversibly sulfated), causing an increase in the internal resistance R_i . For this reason, E occurs more readily in the upper plate areas. It therefore follows that the change to the acid concentration distribution over the height of the plate represents the shifting of the centers of discharge. Furthermore it is possible that the acid sinks more difficultly to the bottom because of the high acid viscosity at low temperatures.

The acid concentration gradients are therefore also the result of inhomogeneous current distribution of the electrodes which is most pronounced at -5 °C (battery 1).

L_{23h} first forms acid stratification in the I-charging-phase (2nd I-phase, Fig. 2a). In the subsequent U charging phase, the stratification is reduced in a similar fashion like during L_{18h} . However, the stratification is not completely eliminated. The extent of reduction varies according to the temperature and over a markedly different timescale (Fig. 2a). At 60 °C, battery 4 shows the highest stratification reduction at the end of L_{23h} and at 3 °C, battery 2 shows the lowest stratification reduction (Table 3 and Fig. 2b). However, battery 4 also shows the largest expansion in stratification (largest local maximum) in the I-charging phase (Fig. 2b), caused by the extreme increase in acid densities at the start of L_{23h} in the lower plate areas. (There is also a sharp increase in acid density in the other batteries, but it is highest at 60 °C.) After the end of the I-charging phase, at 60 °C, acid densities are found at 80% and 100% immersion depth that are greater than 1.30 kg/L. These values decrease in the subsequent hours of L_{23h} , probably caused by gassing. Due to the lower viscosity of the electrolyte at high temperatures, volume elements of higher density should sink more easily

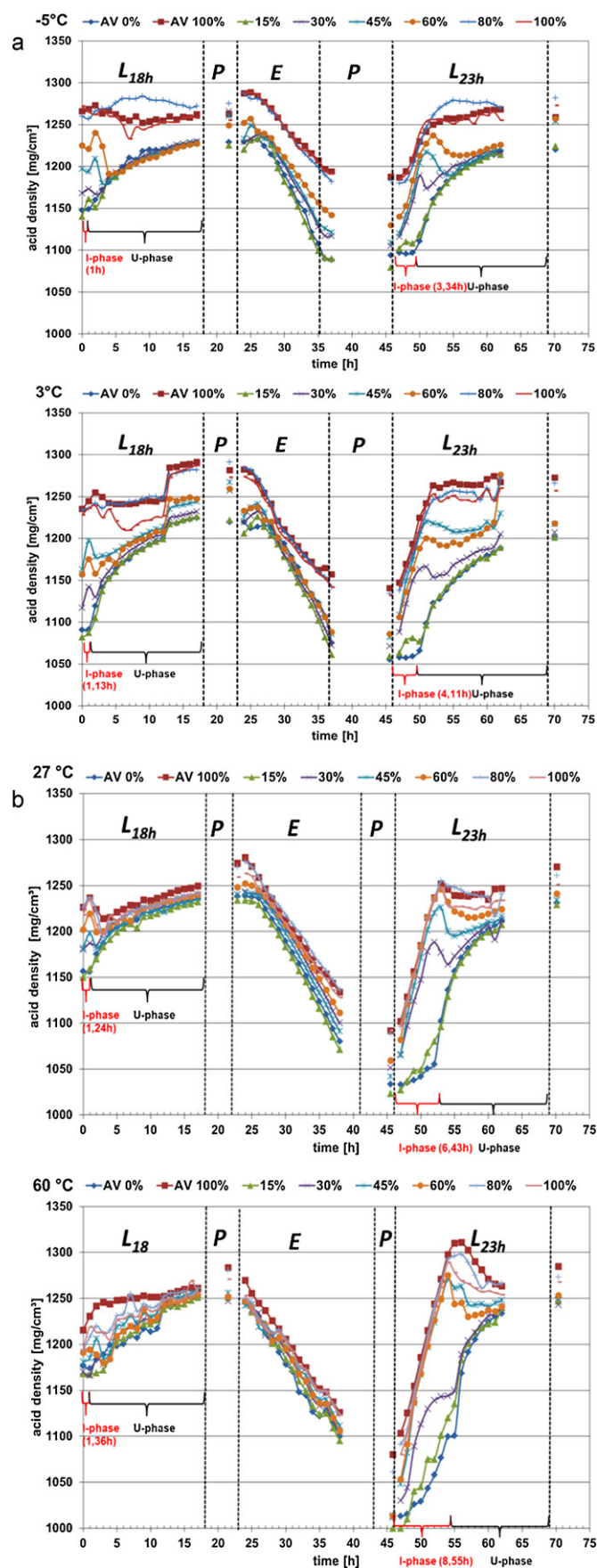


Fig. 2. (a and b) Acid density ρ [mg cm⁻³], measured during L_{18h}, E, and L_{23h} at different plate heights.

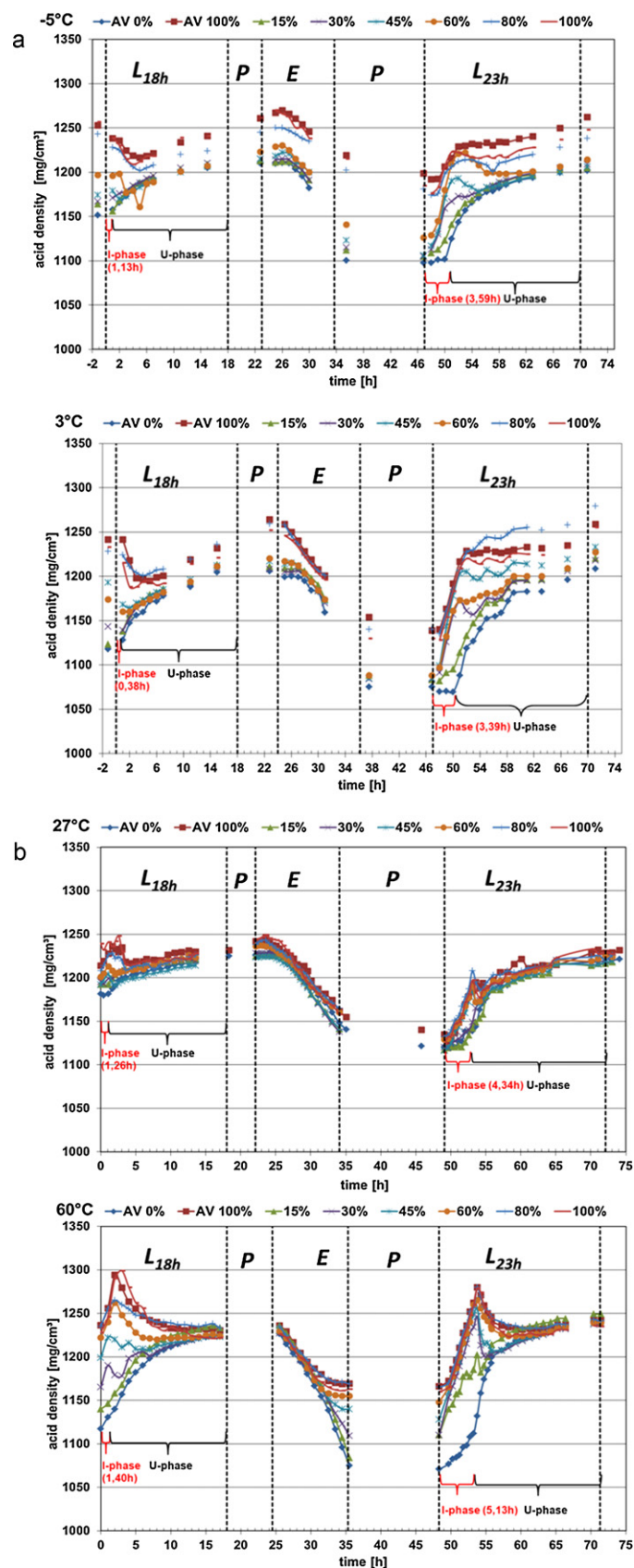


Fig. 3. (a and b) Last CTU: acid density ρ [mg cm⁻³], measured during L_{18h}, E, and L_{23h} at different plate heights.

Table 4
Charging factors during recharging (L_{23h}) and charging factors of L_{23h} in the I-branch.

$T [^{\circ}\text{C}]$	–5	3	27	60
Charging factor	1.202	1.124	1.134	1.160
Charging factor in the I branch	0.585	0.614	0.764	0.895

to the bottom of the cell from the upper areas. However, gassing causes these elements also to be dispersed more easily.

Taking into account the charging factors, which are highest at -5°C (battery 1) and 60°C (battery 4) (Table 4), we can conclude that the predominant reduction in stratification at these temperatures during L_{23h} is caused by increased gassing. The charging factor in the I-branch that increases with the temperature corresponds to the increase in the acid conductivity with the temperature, the increased solubility of the lead sulfate, and the fall in the diffusion overvoltage.

3.2. Formation of acid stratification after the last continuous testing unit

The measurement of the acid densities over the plate heights of the respective sample batteries after the last CTU was performed analogous to the first CTU during the equalization charging L_{18h} , the discharging E , and the recharging L_{23h} in the 17.5% cycle test. Batteries 1, 2, and 4 (-5°C , 3°C , and 60°C) failed after 3 CTUs of the battery cycling described under Section 2.2.2 with 17.5% depth of discharge, while battery 3 (27°C) completed 7 CTUs of the cycle test.

When observing the acid density differences of the last CTU, as with the first CTU, it is evident that stratification occurs in all batteries during the 85 cycles, dependent on the temperature. At temperatures of -5°C , 3°C , and 27°C (batteries 1, 2, and 3), the stratification is more significant in the first CTU than in the last. Only in battery 4 (60°C), stratification was stronger in the last CTU compared to the first CTU.

The stratification of the longest surviving cycled battery, battery 3, cycled at 27°C , is smallest after the last 85 cycles (Table 3). The initial moderate stratification in the electrolyte of battery 3 is obviously reduced quickly, with the result that only a low level of stratification remains at the end of the test (Table 3). During the last unit of the test, battery 3 must have been fully recharged regularly in the previous 85 cycles, causing only slight stratification. At the start of L_{18h} , the acid densities first increase in the mid plate areas while the acid density above initially remains unchanged and there is only a slight acid density increase below. The almost complete reduction in stratification – probably due to the gassing (Fig. 3b) – only occurs after advanced charging time.

In contrast to the batteries 1, 2, and 4 (-5°C , 3°C and 60°C) cycled at other test temperatures, the charging of battery 3 (27°C) L_{18h} and L_{23h} and the discharging E are very uniform over the height of the plates (Fig. 3b). This can be explained by the fact that a stationary condition has been established in battery 3, with regards to the charging and discharging process, after a specific quantity of electrolyte has been consumed and thereby a specific sulfate distribution was established.

In all other batteries, where there are irregularities in the acid density curves during L_{18h} , E , and L_{23h} (Fig. 3a and b), the more uneven local distribution of charging and discharging up to (early) failure, caused by temperature and charging voltage, might prevent a stationary condition from being established. We observed that the acid density curves of the two batteries (1 and 2) tested at low temperatures (-5°C and 3°C) differed significantly from the one tested at 60°C (battery 4). It is significant that, at the start of L_{18h} (shortly after cycling), the acid density differences of all batteries (with the exception of the differences of battery 4) are lower

compared to the first CTU (Table 3). The reason for this is that sulfuric acid is consumed – since it participates in the charging and discharging process. This means that, during the cycles, successively more irreversible lead sulfate is formed during the discharges.

During L_{18h} , the stratification in all batteries decreases as in the first CTU, with the lowest stratification observed at the end of L_{18h} as the temperature increases. The change in stratification during L_{18h} is most pronounced at 60°C (battery 4), followed by 3°C (battery 2), -5°C (battery 1), and 27°C (battery 3) (Table 3 and Fig. 3a and b).

The large increase in acid density differences at the start of L_{18h} for battery 4 (60°C) can be explained by insufficient charging over the height of the plates.

In the case of batteries 1, 2, and 4 (-5°C , 3°C , and 60°C), the acid density differences (Table 3) increase during E . This can be seen in the divergence of the acid density values (Fig. 3a and b). The most significant stratification is found in the electrolyte of battery 1 (-5°C) after E (like in the first CTU) (Table 3). In the last CTU, battery 4 (60°C) has significantly higher stratification after E (Table 3), compared to the first CTU. In battery 3 (27°C), the stratification markedly decreases after E unlike in the first CTU. In battery 2 (3°C), the electrolyte is stratified in the last CTU in a similar way like in the first CTU (Table 3). As in the first CTU, these acid density differences can be explained by increasing inhomogeneity of the electrodes. This entails an increased shifting of the reaction areas over the height of the plate, from bottom to top. For example, the battery cycled at 60°C during E can be significantly discharged in the upper area but hardly at all in the lower area. In the last third of E , the acid density in the lower area does not change any more. Up to the end of E , batteries 1 and 2 (-5°C and 3°C) on the other hand show a significant change in acid density in the lower area of the plates too. However, an increasing shift in the focus of discharge to the middle and upper areas is observed here, too.

During L_{23h} stratification is reduced at temperatures of -5°C , 3°C , and 60°C (batteries 1, 2, and 4) (Table 3). In battery 4 (60°C), we observe very significant stratification formation in the first charging phase and then a very significant reduction in stratification (Fig. 3b). This also levels out the stratification that existed before L_{23h} . This could be explained by an intensive homogenization of the stratification caused by gassing, indicated by the high charging factor in battery 4 (Table 4). The low viscosity of the acid present at high temperatures facilitates the convective reduction of stratification.

At low temperatures, during L_{23h} , the acid density curve is similar to the one found after the first CTU for -5°C (battery 1) and 3°C (battery 2). However, the absolute values of the acid densities at the comparable measuring points are lower. As was the case in the first CTU, a comparable reduction in stratification occurs in the second charging phase after an initial increase in stratification in the first charging phase of L_{23h} . Since high charging factors are found at these temperatures (-5°C , 3°C , batteries 1 and 2), and 60°C , battery 4 (Table 5), we can conclude that the reduction in stratification is mainly caused by gassing. The fact that this stratification reduction at low temperatures (or: for batteries 1 and 2 – we also talk about the charging factor for 60°C in the previous sentence) caused by gassing is much less effective compared with the reduction at high temperatures, we can assume that the higher viscosity of the acid present at low temperatures is the cause. At 27°C (battery 3), there is almost no change in stratification during L_{23h} (Table 3). The small degree of stratification formed during the first charging

Table 5
Charging factors during recharging (L_{23h}).

$T [^{\circ}\text{C}]$	–5	3	27	60
Charging factor	1.16	1.23	1.12	1.29

phase is largely removed by the end of charging (by gassing). At the same time, battery 3 (27 °C) shows the lowest charging factor (Table 5). These findings can be explained by the fact that the plate is charged relatively evenly over the entire height, with the result that this battery shows the lowest current densities and the lowest level of gassing.

4. Summary

The batteries cycled at different temperatures (−5 °C, 3 °C, 27 °C, and 60 °C) with 17.5% depth of discharge show different stratification behavior, depending on the temperature, during cycling, subsequent equalization charging, discharging, and recharging. We can therefore conclude that acid stratification is a result of uneven current distribution over the height of the electrodes. The uneven current distribution is modified by the transport of acid particles in the liquid phase, formed to varying extents in the different plate areas. Acid stratification is consequently a product of discharging as well as a product of charging which modifies the findings in [17,18]. Different temperatures cause different distributions of charging and discharging in the individual areas of the electrodes, thereby causing different local amount of substance. The changing temperatures cause changes in gassing. Gassing, on the other hand, counteracts stratification due to the convective homogenization of the acid. The homogenizing effect of the gassing decreases when the temperature decreases. This is caused by the increasing viscosity of the acid, which reduces homogenization.

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